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Research Article

Selective liquid phase oxidation of cyclohexane over $Pt/CeO_2–ZrO_2–SnO_2/SiO_2$ catalysts with molecular oxygen

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Abstract: Partial oxidation of cyclohexane into cyclohexanone and cyclohexanol (KA-oil) is an industrially significant reaction for producing precursors for the synthesis of ε-caprolactam and adipic acid, which are the building blocks of nylon. However, to date, the cyclohexane conversion ratio has usually been limited to less than 6% to prevent further oxidation of the cyclohexanol and cyclohexanone targets. In this study, we report that $Pt/CeO_2–ZrO_2–SnO_2/SiO_2$, in which $CeO_2–ZrO_2–SnO_2$ provide reactive oxygen molecules from inside the bulk, can act as efficient catalysts. Optimization of the catalyst composition and reaction conditions provided a cyclohexane conversion ratio of 24.1% and a total selectivity for cyclohexanol and cyclohexanone of 83.4% at 130 ℃ in 0.5 MPa (4.9 atm) air for 7 h over a 5wt%Pt/16wt%$Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}/SiO_2$ catalyst. This catalyst has significant advantages over conventional catalysts because the reaction proceeds at a lower pressure, and there is no need for toxic radical initiators or free-radical scavengers.

Keywords: composite materials; oxidation; cyclohexane; KA-oil; catalyst

1 Introduction

The selective oxidation of cyclohexane (CyH) to cyclohexanone (Cy=O, denoted as "K") and cyclohexanol (CyOH, denoted as "A"), which is a radical chain reaction, is a significant process in the chemical industry, because these are important intermediates for the manufacture of nylon-6 and nylon-6,6 [1]. The conventional industrial process for CyH oxidation to a mixture of K and A (known as KA-oil) involves the use of soluble cobalt or manganese salts as homogeneous catalysts that are radical generation agents, and the reaction is conducted at 140–180 ℃ and 0.8–2 MPa (7.9–19.8 atm) in air for 15–60 min [1]. KA-oil is produced by this method with 70%–85% selectivity; however, the CyH conversion ratio is usually limited to less than 6% to prevent further oxidation of the target KA-oil.

A number of alternative processes that employ heterogeneous catalysts have been proposed for selective CyH oxidation using molecular oxygen with a particular focus on improving the CyH conversion ratio without a significant decrease in the selectivity for KA-oil. Catalysts consisting of gold nanoparticles supported on zeolites such as ZSM-5 (Zeolite Socony Mobil No. 5) [2] and MCM-41 (Mobil Composition of Matter No. 41) [3] can convert CyH to KA-oil at 150 ℃ in 1 MPa (9.9 atm) O_2 atmosphere for 2–6 h with a 6%–19% conversion ratio and 92%–100% selectivity, even in the absence of free-radical

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scavengers [4,5]. An Au/SiO_2 catalyst, in which gold nanoparticles were embedded in amorphous silica, also exhibited a high catalytic activity of 22.7% for CyH conversion and 80.6% selectivity for KA-oil at 150 ℃ and 1.5 MPa (14.8 atm) O_2 for 3 h, although toxic and explosive *tert*-butyl hydroperoxide (TBHP) was used as a radical initiator [6]. Size-controlled Au clusters on hydroxyapatite exhibited a CyH conversion ratio of 6.7%–14.9% with 94%–99% selectivity for KA-oil at 150 ℃ under 1 MPa (9.9 atm) O_2 for 4 h [7], although the addition of a small amount of TBHP was also essential in this case to initiate the reaction.

Mesoporous chromium and iron terephthalates (Cr- and Fe-MIL-101, respectively), which are categorized as metal–organic frameworks, have demonstrated high catalytic activity and selectivity for the oxidation of CyH [8]. The Cr-MIL-101/TBHP system produces KA-oil with 92% selectivity at a 25% CyH conversion ratio, while Fe-MIL-101/TBHP/O_2 gives a mixture of cyclohexyl hydroperoxide, K, and A with 99% total selectivity (49% selectivity for KA-oil) and a 38% conversion ratio at 70 ℃ in air (1 atm) for 8 h. However, the addition of TBHP is also essential in these reactions. Fe-filled carbon nanotubes are also active catalysts that have yielded a CyH conversion ratio of about 37% at 125 ℃ and 1.5 MPa (14.8 atm) O_2 for 8 h, although the selectivity to KA-oil was about 30% due to over-oxidation [9].

This situation has prompted the examination of novel and advanced CyH oxidation catalysts that can realize high CyH conversion ratios with high selectivity for KA-oil in a liquid phase reaction. We have previously prepared novel catalysts to realize the complete oxidation of volatile organic compounds under moderate conditions [10,11]. These catalysts involved a combination of platinum and a solid promoter to supply reactive oxygen molecules, which was important in order to allow oxidation of hydrocarbons in the gas phase [11,12]. Complete oxidation of ethylene, toluene, and acetaldehyde was realized at temperatures as low as 55, 110, and 140 ℃, respectively, over a $10wt\%Pt/16wt\%Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}/\gamma\text{-}Al_2O_3$ catalyst [13].

In the present study, we have designed advanced catalysts that are optimized for CyH oxidation to KA-oil in the liquid phase without the need for radical initiators or free-radical scavengers. To realize such advanced catalysts, we have focused on a combination of Pt, $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$, and SiO_2 (silica gel). In this catalyst, platinum acts as the main oxidation agent and the $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$ solid solution is the promoter from which reactive oxygen molecules are provided. Silica gel is employed as a catalyst support instead of $\gamma\text{-}Al_2O_3$ because it has superior adsorption capabilities for C_6 and C_7 hydrocarbons [14]. In this study, $x wt\%Pt/16wt\%Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}/SiO_2$ (hereafter denoted as $Pt(x)/CZS/SiO_2$, where $1 \leqslant x \leqslant 10$) catalysts were prepared and their oxidation activity for the conversion of CyH into K and A was investigated. Furthermore, the catalyst composition was optimized to simultaneously realize high activity and high selectivity.

2 Experiment

2.1 Preparation of the $Pt/CeO_2–ZrO_2–SnO_2/SiO_2$ catalysts

The $16wt\%CZS/SiO_2$ support was synthesized by co-precipitation and impregnation methods. SnC_2O_4 was dissolved in a mixture of 1.0 $mol \cdot L^{-1}$ $Ce(NO_3)_3$ and 0.1 $mol \cdot L^{-1}$ $ZrO(NO_3)_2$ aqueous solutions in a stoichiometric ratio, and the mixture was then impregnated into commercially available silica gel (Fuji Silysia Chemical, CARiACT Q-3). The CZS content was adjusted to 16 wt% of the total support to optimize the amount of promoter available so as to provide the highest oxidation activity [13]. The pH of the aqueous mixture was adjusted to 11 by dropwise adding aqueous ammonia (5%). After stirring for 12 h at room temperature, the resulting precipitate was collected by filtration, washed several times with deionized water, and then dried at 80 ℃ for 12 h. The sample was ground in an agate mortar and then calcined at 600 ℃ for 1 h in the ambient atmosphere. Supported platinum catalysts ($x wt\%Pt/16wt\%Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}/SiO_2$) ($1 \leqslant x \leqslant 10$) were prepared by impregnating the $16wt\%CZS/SiO_2$ support with a 4 wt% platinum colloid aqueous solution stabilized with polyvinylpyrrolidone (Tanaka Kikinzoku Kogyo Co., Ltd.). After impregnation, the sample was dried at 80 ℃ for 6 h and then calcined at 500 ℃ for 4 h. As references, $5wt\%Pt/y wt\%Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}/SiO_2$ catalysts (hereafter denoted as $Pt(5)/CZS(y)/SiO_2$, where $1 \leqslant y \leqslant 30$) were also prepared to identify the feature of CZS.

2. 2 Cyclohexane oxidation

The cyclohexane (CyH) oxidation reaction was conducted in batch mode using a mechanically stirred 50 mL autoclave made from SUS316 stainless steel. Prior to the reaction, CyH (5.0 g) and the catalyst (10 mg) were loaded into the autoclave, and dry air was supplied to the reactor. The reactor was sealed and heated to a stable operational temperature. After the reaction, the products were collected by decantation and analyzed using gas chromatograph mass spectrometry (GCMS; Shimadzu GCMS-QP2010 Plus). The turnover frequency (TOF) is defined as the number of cyclohexane molecules that a catalyst can convert to KA-oil per surface Pt site per unit of time. The amount of Pt atom exposed on the surface (Pt_s) was calculated from the amount of CO chemisorption, assuming that the metallic particles are spherical and one CO molecule adsorbs on one surface platinum atom ($CO/Pt_s = 1$). Accordingly, TOF can be calculated from the following equation:

$$\mathrm{TOF}(\mathrm{h}^{-1}) = \frac{\text{KA-oil synthesis rate}\,(\mathrm{mol}\cdot\mathrm{g}^{-1}\cdot\mathrm{h}^{-1})}{\text{Amount of CO adsorption}\,(\mathrm{mol}\cdot\mathrm{g}^{-1})}$$

2. 3 Characterization

The sample compositions were analyzed using X-ray fluorescence spectrometry (XRF; Rigaku ZSX-100e). The crystal structures of the catalysts were identified by X-ray powder diffraction (XRD; Rigaku SmartLab) analysis using Cu Kα radiation (40 kV, 30 mA). The Brunauer–Emmett–Teller (BET) specific surface areas were measured by nitrogen adsorption at −196 ℃ (Micromeritics Tristar 3000). Transmission electron microscopy (TEM) was performed at an accelerating voltage of 300 kV (Hitachi H-9000NAR). The metal dispersion analysis was carried out using a pulse method at –50 ℃ with 10%CO–He (0.03 mL). The Pt metal dispersion was defined as the following equation, where the amount of surface Pt atoms was calculated from the CO chemisorption values as mentioned above.

$$\text{Dispersion}\,(\%) = \frac{\text{Amount of Pt atoms exposed on the surface}\,(Pt_s)}{\text{Total amount of Pt atoms}\,(Pt)} \times 100$$

3 Results and discussion

3. 1 Characterization of the catalysts

The chemical composition of the samples was confirmed using XRF. The BET specific surface area and platinum dispersion data for the catalysts are summarized in Table 1. The BET specific surface area decreases with increasing platinum content, which may be due to the much larger density of Pt than that of the oxide promoter and support. The platinum dispersion in the catalysts decreases sharply when the amount of platinum becomes higher than 5 wt%, which suggests significant aggregation of the platinum particles. To confirm this, the degree of aggregation of platinum on the Pt(x)/CZS/SiO_2 ($x = 1$, 5, and 7) catalysts was observed using TEM. Figure 1 shows that there are no notable differences between the Pt(1)/CZS/SiO_2 and Pt(5)/CZS/SiO_2 samples, which both have a particle

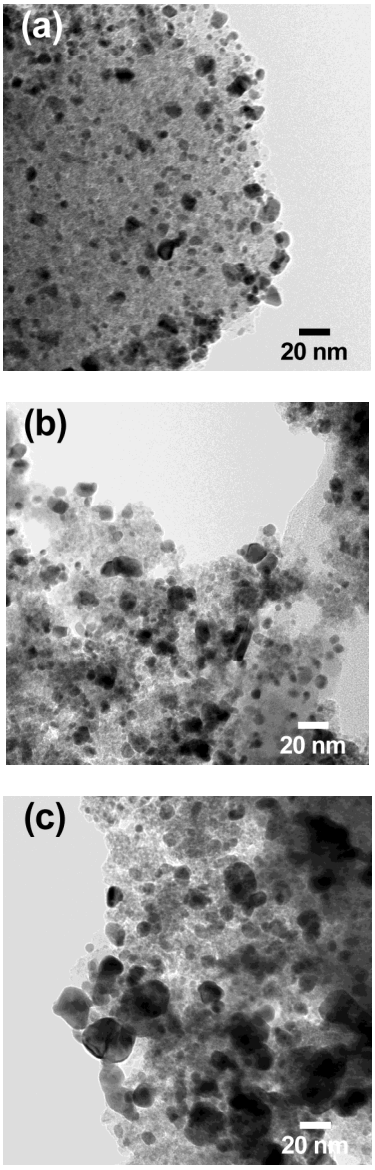

Fig. 1 TEM images of (a) Pt(1)/CZS/SiO_2, (b) Pt(5)/CZS/SiO_2, and (c) Pt(7)/CZS/SiO_2 catalysts for KA-oil synthesis.

Table 1 Catalytic performance of catalysts at 130 ℃ for 7 h in 0.5 MPa air atmosphere

Catalyst*	Surface area ($m^2 \cdot g^{-1}$)	Amount of CO chemisorption ($\mu mol \cdot g^{-1}$)	Total amount of Pt atoms ($\mu mol \cdot g^{-1}$)	Dispersion (%)	Conversion (mol%)	KA-oil yield (mmol)	KA-oil synthesis rate† ($mmol \cdot g^{-1} \cdot h^{-1}$)	Selectivity (mol%)		TOF§ (h^{-1})
								Cyclohexanol	Cyclohexanone	
Pt(1)/CZS/SiO_2	322	11.4	51.3	22.2	15.0	7.84	112	58.7	29.3	9845
Pt(3)/CZS/SiO_2	320	33.2	154	21.6	17.5	8.86	127	56.0	29.2	3810
Pt(5)/CZS/SiO_2	313	48.9	256	19.1	24.1	11.9	171	55.2	28.2	3485
Pt(7)/CZS/SiO_2	290	29.1	359	8.1	15.5	7.77	111	55.4	29.0	3820
Pt(10)/CZS/SiO_2	275	36.4	513	7.1	12.6	6.42	92	55.6	30.1	2518

*Pt content was determined by XRF. †Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 130 ℃, 0.5 MPa, and 7 h. §TOF was calculated from the rate of KA-oil (cyclohexanol and cyclohexanol) synthesis divided by the amount of CO molecules chemisorbed on the Pt surfaces.

size of approximately 10 nm. In contrast, a number of large platinum particles are observed for the Pt(7)/CZS/SiO_2 catalyst, which is consistent with the results of the BET surface area measurements.

Figure 2 shows XRD patterns for the Pt(x)/CZS/SiO_2 ($1 \leqslant x \leqslant 10$) catalysts. Only peaks corresponding to platinum, cubic fluorite-type oxide, and amorphous SiO_2 appear, and no crystalline impurities are observed. The positions of the peaks assigned to the cubic fluorite structure are the same for all of the samples, which indicates that the platinum is simply supported on the CZS/SiO_2 surface, and does not form a solid solution with CZS or SiO_2.

3. 2 Catalytic performance

The catalytic performance for the selective oxidation of CyH over the Pt(x)/CZS/SiO_2 catalysts was investigated in an air atmosphere (Table 1). Highly efficient and quantitative CyH oxidation to KA-oil could be accomplished at 130 ℃ for 7 h under a 0.5 MPa (4.9 atm) air atmosphere for all samples. Even without the use of radical initiators and free-radical scavengers, the results for both conversion and selectivity are excellent. In particular, the reaction pressure (0.5 MPa or 4.9 atm) employed in the catalytic system is significantly lower than that used with conventional methods (1–1.5 MPa or 9.9–14.8 atm) [4–9]. The highest activity is obtained for Pt(5)/CZS/SiO_2, for which a conversion ratio of 24.1% and a selectivity of 83.4% for KA-oil are achieved. The slight decrease in the conversion ratio for high Pt concentrations may be due to the large amount of aggregation of the Pt particles.

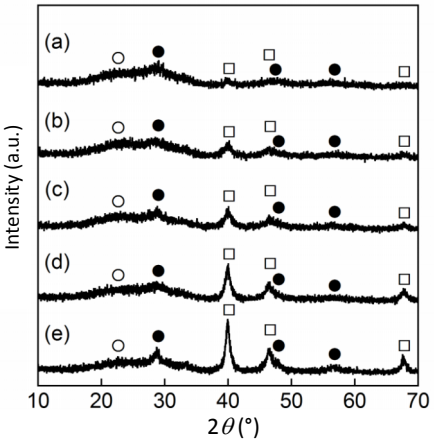

Fig. 2 XRD patterns for (a) Pt(1)/CZS/SiO_2, (b) Pt(3)/CZS/SiO_2, (c) Pt(5)/CZS/SiO_2, (d) Pt(7)/CZS/SiO_2, and (e) Pt(10)/CZS/SiO_2 catalysts (□: Pt, ●:CZS, ○: SiO_2).

Figure 3(a) shows the dependence of the CyH conversion ratio and the KA-oil selectivity on the reaction pressure for the Pt(5)/CZS/SiO_2 catalyst, where the reaction temperature and time are fixed at 130 ℃ and 7 h, respectively. The CyH conversion ratio is improved by the application of pressure and the highest selectivity for KA-oil is obtained at 0.5 MPa (4.9 atm). However, the selectivity decreases as the pressure is increased further due to the over-oxidation of CyH into by-products such as pentanoic acid, glutaric acid, and carbon dioxide. Figure 3(b) shows the influence of the reaction temperature; the conversion ratio becomes saturated at 130 ℃ and is virtually constant at higher temperatures. However, the total selectivity for KA-oil decreases with increasing temperature. Figure 3(c) depicts the effect of the reaction time on the CyH conversion ratio and KA-oil selectivity for the Pt(5)/CZS/SiO_2 catalyst. The CyH oxidation reaction progresses from 3 to 12 h, and a conversion ratio of 24.1% and a selectivity of 83.4% for the two desired oxygenates are achieved at 7 h. Similar to previously reported results [6], the oxidation reaction does not appear to slow down with time, which indicates that there is no loss of catalytic activity. However, the selectivity for KA-oil decreases with increasing reaction time due to over-oxidation of CyH. The detailed results are summarized in Table 2.

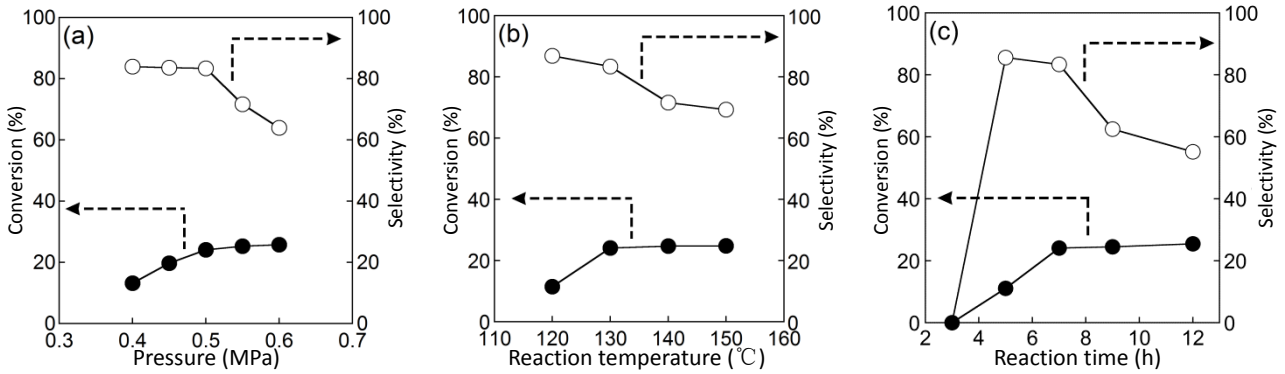

Fig. 3 Catalytic performance of the Pt(5)/CZS/SiO_2 catalyst. (a) Effect of reaction pressure on CyH conversion and selectivity for KA-oil (CyOH and Cy=O). Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 130 ℃, and 7 h. (b) Effect of reaction temperature. Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 0.5 MPa (4.9 atm), and 7 h. (c) Effect of reaction time. Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 130 ℃, and 0.5 MPa (4.9 atm).

Table 2 Catalytic performance of the Pt(5)/CZS/SiO_2 catalyst under various reaction conditions

Pressure (MPa)	Temperature (℃)	Reaction time (h)	Conversion (mol%)	KA-oil yield (mmol)	KA-oil synthesis rate‡ (mmol·g^{-1}·h^{-1})	Selectivity(mol%)		TOF§ (h^{-1})
						Cyclo-hexanol	Cyclo-hexanone	
0.3	130	7	0	0	0	0	0	0
0.4			13.2	6.74	96	56.6	29.4	1968
0.45			19.7	9.90	141	55.3	29.3	2889
0.5			24.1	11.9	171	55.2	28.2	3485
0.55			25.3	11.9	170	51.3	27.8	3470
0.6			25.8	9.81	140	40.0	24.0	2863
0.5	120	7	11.5	5.94	85	56.5	30.4	1733
	130		24.1	11.9	171	55.2	28.2	3485
	140		24.7	10.5	150	51.0	20.6	3066
	150		24.8	10.2	146	48.8	20.5	2980
0.5	130	3	0	0	0	0	0	0
		5	11.1	5.64	113	54.1	31.5	2306
		7	24.1	11.9	171	55.2	28.2	3485
		9	24.5	9.10	101	39.1	23.4	2065
		12	25.5	8.36	70	35.6	19.6	1424

‡Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane. §TOF was calculated from the rate of KA-oil (cyclohexanol and cyclohexanol) synthesis divided by the number of CO molecules chemisorbed on the Pt surfaces.

To identify the feature of CZS, Pt(5)/CZS(y)/SiO_2 $1 \leqslant y \leqslant 30$ catalysts were also prepared and their catalytic activities were evaluated. Dependence of the catalytic performance of the Pt(5)/CZS(y)/SiO_2 catalysts on the amount of CZS is shown in Fig. 4, where the reaction conditions are 10 mg catalyst, 5.0 g cyclohexane, 130 ℃, 0.5 MPa (4.9 atm), and 7 h. The CyH conversion increases with increasing the amount of CZS. The KA-oil selectivity is almost maintained until $y = 16$, but it gradually decreases when an excess amount of CZS is loaded on the catalyst due to over-oxidation. From these results, the feature of CZS is evidenced that appropriate amount of CZS addition is effective to increase the CyH conversion without decreasing the KA-oil selectivity.

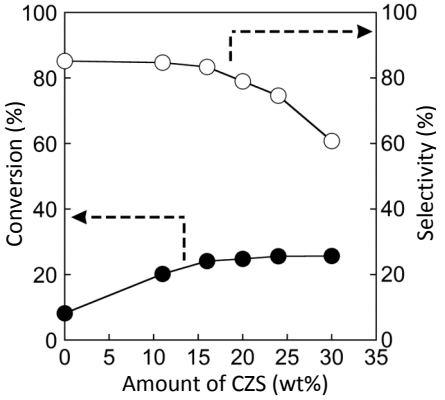

Fig. 4 Dependence of the catalytic performance of Pt(5)/CZS(y)/SiO_2 ($0 \leqslant y \leqslant 30$) catalysts on the amount of CZS. Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 130 ℃, 0.5 MPa (4.9 atm), and 7 h.

Figure 5 presents the relationship between the CyH conversion ratio and the selectivity for KA-oil under various reaction conditions for all of the catalysts in the present study. The selectivity for KA-oil decreases very gradually with increasing CyH conversion ratio until it reaches 24.1%. However, when the conversion ratio becomes greater than 24.1%, the selectivity decreases sharply due to over-oxidation. Therefore, it is crucial to limit the conversion ratio to just below this threshold in order to satisfy the requirements of both a high conversion ratio and high selectivity. Based on the results shown in Fig. 4, the optimum reaction conditions for obtaining the highest yield of KA-oil are 0.5 MPa (4.9 atm), 130 ℃, and 7 h with the Pt(5)/CZS/SiO_2 catalyst, for which 24.1% CyH conversion ratio and 83.4% selectivity are simultaneously realized. Furthermore, even though the catalysis test is repeated five times under the same conditions, the catalyst remains stable and no change is found in either the activity or selectivity.

3. 3 Reaction mechanism

The CyH oxidation reaction proceeds via the free radical chain mechanism indicated in reactions (1) to (5) [15,16]:

$$CyOOH \rightarrow CyO^{\bullet} + {}^{\bullet}OH \quad (1)$$

$$CyO^{\bullet} + CyH \rightarrow CyOH + Cy^{\bullet} \quad (2)$$

$$Cy^{\bullet} + O_2 \rightarrow CyOO^{\bullet} \quad (3)$$

$$CyOO^{\bullet} + CyH \rightarrow CyOOH + Cy^{\bullet} \quad (4)$$

$$2CyOO^{\bullet} \rightarrow CyOH + Cy{=}O + O_2 \quad (5)$$

The chain reaction is initiated by homolytic bond cleavage of cyclohexyl hydroperoxide (CyOOH) according to reaction (1). Cerium ions can exhibit redox activity between Ce^{3+} and Ce^{4+}, and thereby this initiation is catalyzed via the Haber–Weiss cycle [17]. The $CyO^{\bullet}$ radical produced by reaction (1) reacts with CyH via reaction (2) to form the cyclohexyl radical ($Cy^{\bullet}$). This then rapidly reacts with molecular O_2 to form the cyclohexyl peroxy radical ($CyOO^{\bullet}$) according to reaction (3), and the $Cy^{\bullet}$ radical is then continuously regenerated in reaction (4). The formation of CyOH and Cy=O has been attributed to chain termination by mutual destruction of two $CyOO^{\bullet}$ radicals according to reaction (5) [16,17].

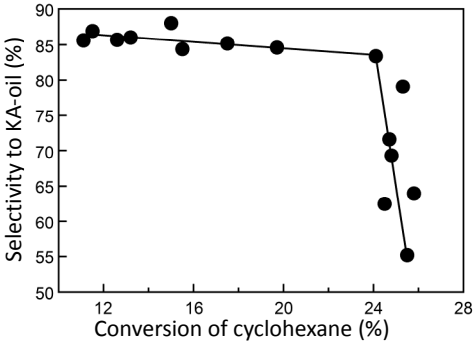

Fig. 5 Relationship between CyH conversion ratio and selectivity for KA-oil. Reaction conditions: 10 mg catalyst, 5.0 g cyclohexane, 0.4−0.6 MPa (3.9−5.9 atm), 120−150 ℃, and 5−12 h.

The selectivity of CyOOH typically decreases with increasing conversion ratio [4]. Under the present reaction conditions, CyOOH is not detected in the products, because it decomposes into CyOH and Cy=O by the radical chain reaction. However, in the reaction mechanism shown in (1) to (5), CyOOH must be produced as the starting material. Since the present process does not involve a radical initiator, CyOOH is expected to be produced by catalytic oxidation of CyH [18,19], so that CyOOH formation is the rate-determining step [20]. In fact, there is an induction period for about 3 h, then the activity increases almost linearly until 7 h, and finally, it saturates after longer than 7 h due to over-oxidation, as seen in Fig. 3(c). This oxidation reaction is facilitated by the readily reducible $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$, which can provide active oxygen species from the catalyst bulk. This oxygen then reacts with CyH at the interface of the Pt and $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$ phases [11,13]. The Pt(5)/CZS/SiO_2 catalyst has a significantly high oxidation activity, so that there is no need for a radical initiator. However, for high CyH conversion ratios, both Cy=O and CyOH are further oxidized, and the selectivities for Cy=O and CyOH are consequently reduced. As a result, there are optimum reaction conditions for balancing both the selectivity and conversion ratio.

4 Conclusions

Novel Pt/CeO_2–ZrO_2–SnO_2/SiO_2 catalysts were successfully prepared for the partial oxidation of CyH into CyOH and Cy=O. The composition was optimized to simultaneously achieve both a high conversion ratio and a high selectivity; a cyclohexane conversion ratio of 24.1% and a selectivity of 83.4% for KA-oil were realized at 0.5 MPa (4.9 atm), 130 ℃, and 7 h using the 5wt%Pt/16wt%$Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$/$SiO_2$ catalyst. This catalytic process has significant advantages in that

not only are radical initiators and free-radical scavengers not required, but also the reaction pressure is significantly lower than that typically applied in conventional reactions, due to the combination of catalytic oxidation by platinum, oxygen provision from the bulk of the CZS promoter, and the adsorption of C6 hydrocarbons onto SiO_2. These characteristics make 5wt%Pt/16wt%$Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$/$SiO_2$ an efficient partial oxidation catalyst for conversion of CyH.

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References

[1] Musser MT. Cyclohexanol and cyclohexanone. In *Ullmann's Encyclopedia of Industrial Chemistry*, *Vol. 11*. Weinheim: Wiley-VCH, 2012: 49–60.

[2] Kokotailo GT, Lawton SL, Olson DH, *et al*. Structure of synthetic zeolite ZSM-5. *Nature* 1978, **272**: 437–438.

[3] Kresge CT, Leonowicz ME, Roth WJ, *et al*. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 1992, **359**: 710–712.

[4] Zhao R, Ji D, Lv G, *et al*. A highly efficient oxidation of cyclohexane over Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant. *Chem Commun* 2004, **40**: 904–905.

[5] Lü G, Zhao R, Qian G, *et al*. A highly efficient catalyst Au/MCM-41 for selective oxidation cyclohexane using oxygen. *Catal Lett* 2004, **97**: 115–118.

[6] Wang C, Chen L, Qi Z. One-pot synthesis of gold nanoparticles embedded in silica for cyclohexane oxidation. *Catal Sci Technol* 2013, **3**: 1123–1128.

[7] Liu Y, Tsunoyama H, Akita T, *et al.* Aerobic oxidation of cyclohexane catalyzed by size-controlled Au clusters on hydroxyapatite: Size effect in the sub-2 nm regime. *ACS Catal* 2011, **1**: 2–6.

[8] Maksimchuk NV, Kovalenko KA, Fedin VP, *et al*. Cyclohexane selective oxidation over metal–organic frameworks of MIL-101 family: Superior catalytic activity and selectivity. *Chem Commun* 2012, **48**: 6812–6814.

[9] Yang X, Yu H, Peng F, *et al*. Confined iron nanowires enhance the catalytic activity of carbon nanotubes in the aerobic oxidation of cyclohexane. *ChemSusChem* 2012, **5**: 1213–1217.

[10] Imanaka N, Masui T. Advanced materials for environmental catalysts. *Chem Rec* 2009, **9**: 40–50.

[11] Imanaka N, Masui T, Yasuda K. Environmental catalysts for complete oxidation of volatile organic compounds and methane. *Chem Lett* 2011, **40**: 780–785.

[12] Yasuda K, Masui T, Imanaka N. Complete oxidation of volatile organic compounds at moderate temperatures. In *Hazardous Materials*: *Types, Risks and Control*. Brar SK, Ed. New York: Nova Science Publishers, 2011: 424–431.

[13] Yasuda K, Yoshimura A, Katsuma A, *et al*. Low-temperature complete combustion of volatile organic compounds over novel Pt/CeO_2–ZrO_2–SnO_2/γ-Al_2O_3 catalysts. *B Chem Soc Jpn* 2012, **85**: 522–526.

[14] Suzuki H. Recovery of hydrocarbons from natural gas. *Oil Gas Business Environ Res* 1978, **11**: 95–103.

[15] Hereijgers BPC, Weckhuysen BM. Aerobic oxidation of cyclohexane by gold-based catalysts: New mechanistic insight by thorough product analysis. *J Catal* 2010, **270**: 16–25.

[16] Tolman CA, Druliner JD, Nappa MJ, *et al*. Alkane oxidation studies in du Pont's central research department. In *Activation and Functionalization of Alkanes*. Hill CL, Ed. Chichester: Wiley, 1989: 303–360.

[17] Sheldon RA, Kochi JK. *Metal-Catalyzed Oxidations of Organic Compounds*. New York: Academic Press, 1981.

[18] Ramanathan A, Hamdy MS, Parton R, *et al*. Co-TUD-1 catalysed aerobic oxidation of cyclohexane. *Appl Catal A*: *Gen* 2009, **355**: 78–82.

[19] Xu LX, He CH, Zhu MQ, *et al*. A highly active Au/Al_2O_3 catalyst for cyclohexane oxidation using molecular oxygen. *Catal Lett* 2007, **114**: 202–205.

[20] Pohorecki R, Bałdyga J. Moniuk W, *et al*. Kinetic model of cyclohexane oxidation. *Chem Eng Sci* 2001, **56**: 1285–1291.